

Synthesis and Characterization of Electrochromic Polyimides

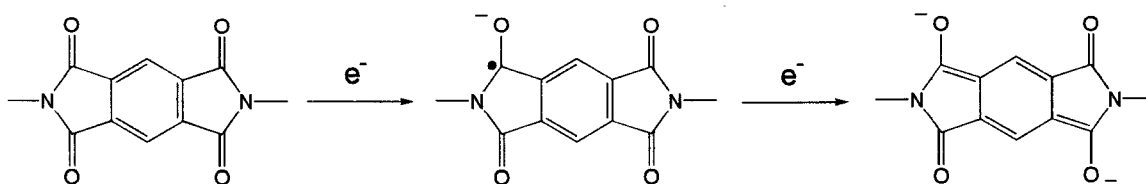
Zhi Yuan WANG, Hai Bin ZHENG, Wen LU, Xian Sheng MENG, Pierre DESJARDINS,

Jian Ping GAO and Yu QI

Department of Chemistry, Carleton University, Ottawa, Canada K1S 5B6

Tel +613-520-2713, Fax +613-5202316, wangw@ccs.carleton.ca

Following the initial work by Haushalter and Krause,¹ the redox properties of some common phthalimides and naphthalimides as well as phthalimide polymers have been described.^{2,3} Owing to its electron affinity, an imide can undergo the electrochemical reduction. The redox mechanism associated with the reduction of pyromellitic diimide has been proposed (Scheme 1).^{2a} The first redox couple corresponds to reduction of the neutral form to the radical anion and the second redox couple relates to further reduction of radical anion to the dianion state. In most cases, imide compounds undergo color changes upon electrochemical reduction or are electrochromic (EC). It is known that the redox potentials can be greatly influenced by the aromatic imide structures.^{3a} The potential of the first reduction shifts anodically as the π -conjugation between two imide groups increases, as seen for naphthalene, perylene, terrylene and quaterrylene diimides.⁴ Radical anion radicals generated from naphthalene diimides are also shown to form π -stacked dimers and oligomers.^{4b,c}



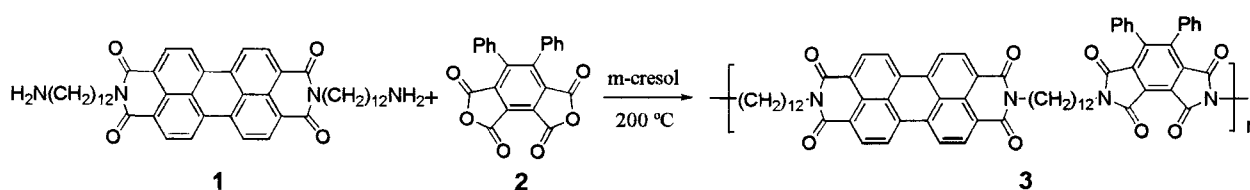
Scheme 1. Proposed mechanism for electrochemical redox reaction of pyromellitic diimide.

Imides and polyimides are traditionally used as dyes (e.g., perylene and naphthalene imide dyes), photoconductors (e.g., perylene diimides) and structural materials (e.g., Kapton polyimide film). Understanding the relationship between the structure, redox property and electrochromism of both small imides and polyimides would allow for exploring the use of these materials in information technology such as display device and security device. Considering the requirement for device fabrication and material processing, we focus on the development of

polyimides that are electrochromic and soluble in common organic solvents. Between six-membered cyclic naphthalimides and five-membered cyclic phthalimides, the former is less common but shows some unique electrochemical properties. Herein, we describe three EC polymer systems containing (1) perylene diimide, (2) bisnaphthalimide and (3) naphthalimide.

Polymer Synthesis

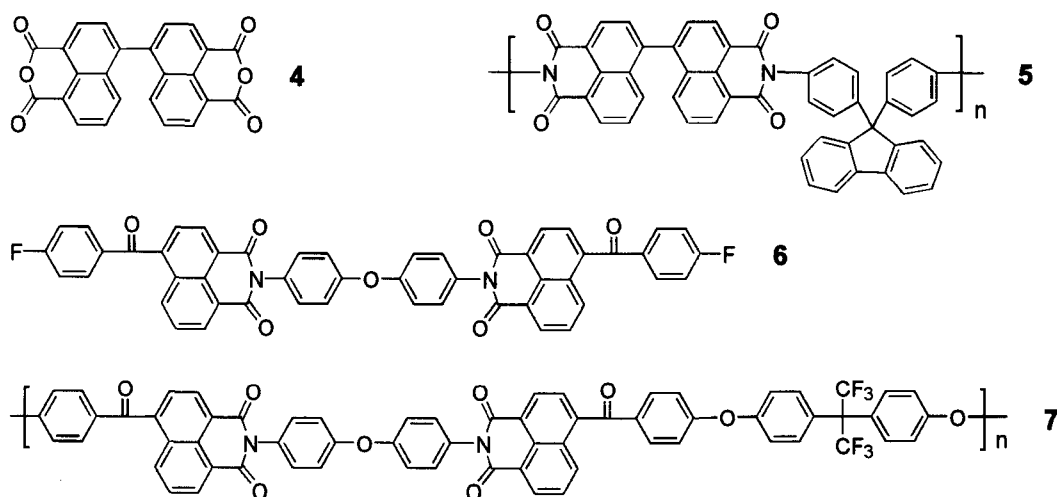
We previously reported the synthesis, characterization and xerographic electrical property of perylene-containing polyimides.⁵ Polyimides derived from perylene dianhydride and aromatic or aliphatic diamines are difficult to obtain in high molecular weight and insoluble in organic solvents except sulfuric acid. Copolymerization using another dianhydride can not produce high molecular weight, soluble, random copolyimides, because insoluble short blocks of perylene imide were formed at the early stage of copolymerization. We have found that perfectly alternating copolyimides are much more soluble (e.g., in *m*-cresol) and can be made in high molecular weight. Thus, polyimide **3** was made by polymerization of diamine **1** and dianhydride **2**. The bent structure of dianhydride **2** is able to impart greater solubility to the resulting polyimide than other commercially available dianhydride (e.g., PMDA and BTDA). Polyimide **3** was found to be soluble in *m*-cresol and hot 1,1,2,2-tetrachloroethane and free-standing film or film on electrodes can be cast from its solution.



Scheme 2. Synthesis of soluble, alternating perylene-based copolyimide.

Two other types of polyimides are represented as polymers **5** and **7**. The former was synthesized from a binaphthyl dianhydride (**4**) and a diamine,⁶ the latter was prepared by polycondensation of the naphthalimide-containing difluoride (e.g., **6**) and a bisphenol (e.g., 6F-BPA).⁷ Polyimides **5** and **7** were readily soluble in many organic solvents such as chloroform and DMF and can be processed to form thin films on Pt or ITO electrodes by casting, spray coating or spin coating. In addition to good solubility, three representative polyimides (**3**, **5** and

7) exhibit excellent thermal stability ($T_g > 250\text{ }^\circ\text{C}$, $T_d > 400\text{ }^\circ\text{C}$) and high mechanical strength ($E' > 2\text{ GPa}$).



Electrochemical Characterization

All three polyimides are electroactive and electrochromic. Cyclic voltammograms (CV) of the electrodes coated with polyimides 3, 5 and 7 were obtained in the electrolyte solution of 0.1 M Bu_4NClO_4 (Figure 1).

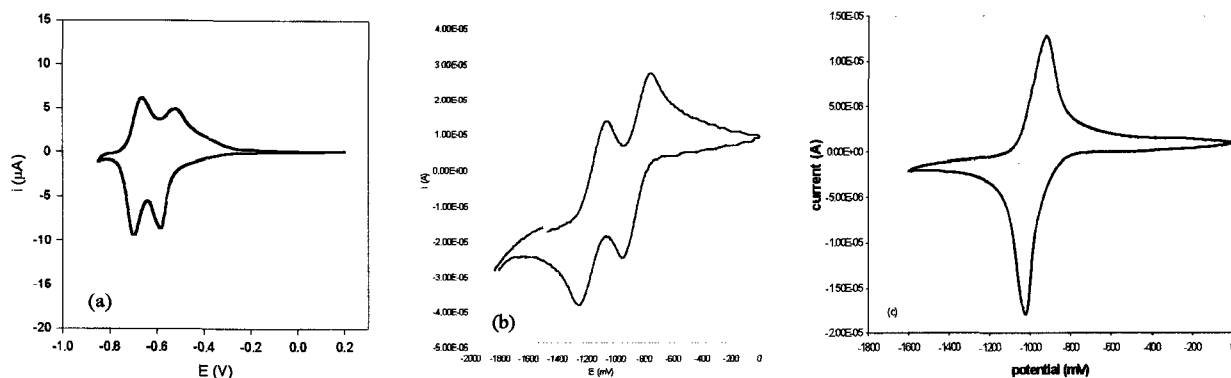


Figure 1. Cyclic voltammograms of (a): copolyimide 3 coated on Pt electrode in acetonitrile with a scan rate of 50 mV/s, (b): polymer 7 coated Pt electrode in propylene carbonate with a scan rate of 100 mV/s, and (c): polyimide 5 coated on Pt electrode in propylene carbonate with a scan rate of 100 mV/s.

At the potential less negative than -0.90 V, two pairs of stable and reversible reduction/oxidation peaks were obtained for polymer **3** (Figure 1a). The similar peak positions were found for the perylene diimides and the corresponding polyimides, proving that the perylene imide unit, rather than the phthalimide unit, in the polymers (e.g., **3**) is responsible for the observed electrochemical activity. Polymer **7** also displayed two pairs of redox peaks (Figure 1b). By comparing the CV of related small molecules, the second reduction peak at the more negative potential is attributed to the reduction of the ketone group presented in polymer **7**. Polynaphthalimide **5** showed only one pair of redox peak with a reduction potential near -1.0 V. It can be seen that the first reduction potential is directly related to extended π -conjugation and electronegativity of the naphthalimide moiety. The perylene imide is more prone to electrochemical reduction than other non-perylene imides such as phthalimide. Having an electron-withdrawing group can lower the reduction potential of the naphthalimide, as evidenced by polymers **5** and **7** (containing a keto group). The similar observation was previously found for the polyimides derived from PMDA and diamines,⁸ where the diamine unit can affect on the reduction potentials (especially the first reduction).

Further scanning the potential more negatively up to -1.80 V, the additional electrochemical reduction responses were observed for polymer **3**. This response could be contributed by reduction of other non-perylene imide units. In general, the phthalimide units produced only one irreversible reduction peak. The irreversibility is likely due to the fact that the phthalimide units are lack of extended π -conjugation.

As shown in Figure 2, once reduced to the radical anion form, the red film of polyimide **3** turned to blue. The original absorbance peaks at 480 and 540 nm decreased; at the same time peaks at 610, 715 and 800 nm appeared and increased gradually. Further reduction caused a decay of the peaks at longer wavelengths and appearance of the peaks at shorter wavelengths, accompanied by a color change from blue to violet. By applying a very cathodic potential of -1.80 V where the non-perylene imide can be reduced, the violet color of polymer film did not change (Figure 2 on left, traces d and e). If an extremely anodic potential of +2.20 V was applied, due to the irreversible oxidation of the perylene moiety, the polymer film would stay in red and not be able to change its color under subsequent negative potentials. Polyimide **7** is also electrochromic, being colorless in its neutral state and red in the reduced form at relatively low

cathodic potential (-1.3 V, Figure 2 on right, traces a and b). At -1.3 V potential, polyimide 7 is also near IR active, showing a peak around 850 nm. Upon further reduction, polyimide 7 appeared to be darker with a new peak showing at 650 nm (traces c-f, Figure 2 on left). Since anodically coloring polyaniline turns to blue upon oxidation, together with use of polyimide 7, a black-and-white, high-contrast, solid EC display device can be realized.

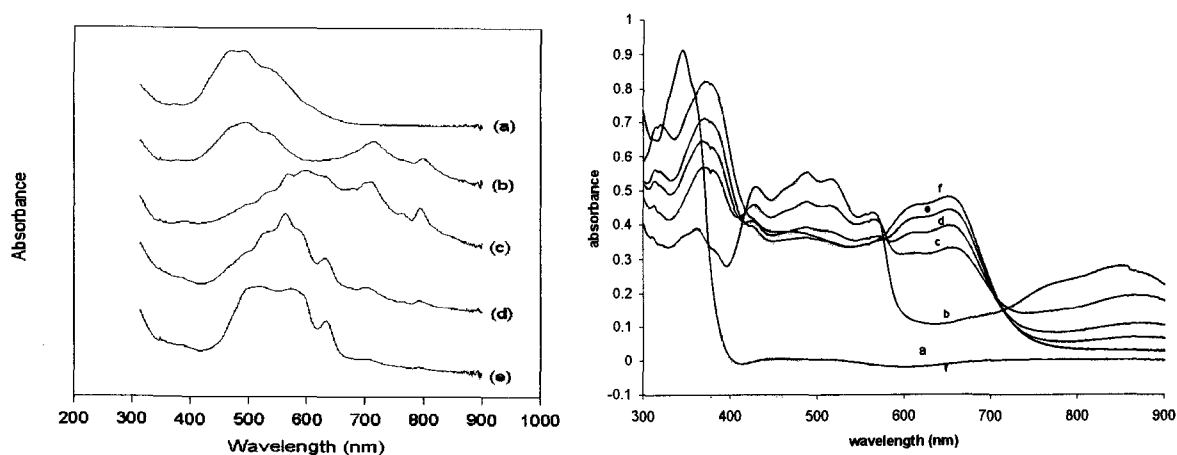


Figure 2. On left: In-situ UV-Vis spectra of polyimide 3 coated on ITO glass electrode, in acetonitrile containing 0.1 M Bu_4NClO_4 . (a) Neutral, (b) -0.55 V, (c) -0.65 V, (d) -0.90 V, (e) -1.80 V. On right: In-situ UV-Vis spectra of polymer 7 coated ITO glass electrode in 0.1 M propylene carbonate containing 0.1 M Bu_4NClO_4 . (a) Neutral, (b) -1.3 V, (c) -1.5 V, (d) -1.7 V, (e) -1.9 V, (f) -2.1 V.

References

1. Haushalter, R.C.; Kraus, L.J. *Thin Solid Films* **1983**, *102*, 161.
2. (a) Mazur, S.; Lugg, P.S.; Yarnilzky, C. *J. Electrochem. Soc.* **1987**, *134*, 346. (b) Krause, L.J.; Lugg, P.S.; Speckhard, T.A. *J. Electrochem. Soc.* **1989**, *136*, 1379.
3. (a) Viehbeck, A.; Gddberg, M.J.; Kovac, C.A. *J. Electrochem. Soc.* **1990**, *137*, 1460. (b) Kwan, W. S. V.; Atanasoska, L.; Miller, L. L. *Langmuir* **1991**, *7*, 1419. (c) Cammarata, V.; Atanasoska, L.; Miller, L. L.; Kolaskie, C. J.; Stallman, B. J. *Langmuir* **1992**, *8*, 876. (d) Kwan, W. S. V.; Penneau, J. F.; Miller, L. L. *J. Electrochem. Chem.* **1990**, *291*, 295. (e) Kwan, W. S. V.; Cammarata, V.; Miller, L. L.; Hill, M. G. *Langmuir* **1992**, *8*, 3003.
4. (a) Lee, S. W.; Zu, Y.; Herrmann, A.; Geerts, Y.; Müllen, K.; Bard, A. J. *J. Am. Chem. Soc.* **1999**, *121*, 3513. (b) Penneau, J. F.; Stallman, B.; Kasai, P. H.; Miller, L. L. *Chem. Mater.*

- 1991, 3, 791. (c) Wang, L.; Goodloe, G. W.; Stallman, B. J. Cammarata, V. *Chem. Mater.* **1996**, 8, 1175.
5. Wang, Z. Y.; Qi, Y.; Gao, J. P.; Sacripante, G.G.; Sundararajan, P.R.; Duff, J.D. *Macromolecules* **1998**, 31, 2075.
6. Gao, J. P.; Wang, Z. Y. *J. Polym. Sci., Part A: Polym. Chem.*, **1995**, 33, 1627.
7. Zheng, H. B.; Wang, Z. Y. *J. Polym. Sci., Part A: Polym. Chem.*, **1999**, 37, 3227.
8. (a) Mazur, S.; Lugg, P.S.; Yarnilzky, C. *J. Electrochem. Soc.* **1987**, 134, 346. (b) Krause, L.J.; Lugg, P.S.; Speckhard, T.A. *J. Electrochem. Soc.* **1989**, 136, 1379.